Journal of Saudi Chemical Society (2013) **17**, 53–59

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Impedance spectroscopic study of corrosion inhibition of Al-Pure by organic Schiff base in hydrochloric acid

A.S. Patel, V.A. Panchal, G.V. Mudaliar, N.K. Shah *

Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad-09, Gujarat, India

Received 31 March 2011; accepted 6 June 2011
Available online 20 July 2011

KEYWORDS

Al-Pure;
HCl;
Electrochemical impedance spectroscopy (EIS);
Inhibitor;
Corrosion

Abstract A new corrosion inhibitor namely o-Chloroaniline-N-benzylidene (o-CANB) has been synthesized and its inhibitive performance toward the corrosion of Al-Pure in 1.0 M hydrochloric acid has been investigated. Corrosion inhibition was studied by chemical method (weight loss) and electrochemical techniques including polarization method and electrochemical impedance spectroscopy (EIS). The present study has shown that this inhibitor is good in acidic media and the inhibition efficiency up to >99% in 1.0 M HCl. Polarization measurement revealed that the investigated inhibitor is a mixed type with a predominant action on cathode. Impedance measurement showed that the charge transfer resistance (R_{ct}) increased and double layer capacitance (C_{dl}) decreased with an increase in the inhibitor's concentration. Obtained results about inhibition efficiency from weight loss, polarization study and EIS are in good agreement with each other. The adsorption of the inhibitor on the metal surface in the acid solution was found to obey Langmuir's adsorption isotherm.

1. Introduction

Corrosion is defined as the deterioration of a material, usually a metal, because of its reaction with the environment and which requires the presence of an anode, a cathode, an electrolyte and an electrical circuit (Rosliza et al., 2010).

Al-Pure and its alloys are important materials due to their high technological value and wide range of industrial applications, especially in aerospace, household industries, and commonly used in marine applications as well. In addition, they are justified by low price, high electrical capacity and high energy density (Addel-Gaber et al., 2006).

The most important feature of aluminium is its corrosion resistance due to the presence of a thin, adherent and protective surface oxide film. Because of this advantage Al-Pure and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries.

* Corresponding author. Tel.: +91 079 26305037, mobile: +91 9825312095.
E-mail addresses: aeshapatelphd@gmail.com (A.S. Patel), vidhipanchal@gmail.com (V.A. Panchal), nishchem2004@yahoo.co.in (N.K. Shah).

Peer review under responsibility of King Saud University.
doi:10.1016/j.jscs.2011.06.003

Production and hosting by Elsevier

Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching of aluminium. Under these circumstances, corrosion inhibitors should be used because the solubility of the oxide film increases above and below the pH 4–9 range and aluminium exhibits a uniform attack (Pourbaix, 1966). Inhibitors are used to prevent metal dissolution and minimize acid consumption. Most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulfur or oxygen atoms in their structure. Despite the large number of organic compounds, there is always a need for developing new organic corrosion inhibitors (Desai et al., 1986; Abd El-Maksoud, 2002; Ajmal et al., 1994).

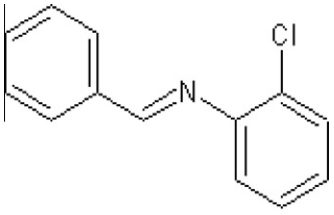
Some Schiff bases have recently reported as effective corrosion inhibitors for steel (Bain et al., 1989; Emregul et al., 2003), aluminium (Gomma and Wahdan, 1995), aluminium alloys (Hahner et al., 1993) and copper (Li et al., 1999) in acidic media. Due to the presence of –C═N– group, an electron cloud on the aromatic ring, the electronegative nitrogen, oxygen and sulfur atoms in the molecule, Schiff bases should be good corrosion inhibitors (Aytac et al., 2005). The action of such inhibitors depends on the specific interaction between the functional groups and the metal surface. So it is very important to clarify the interactions between the inhibitor molecules and metal surfaces in order to search new and efficient corrosion inhibitors (Yurt et al., 2006).

In the earlier work the inhibition of corrosion of zinc in sulfuric acid by the Schiff bases of ethylenediamine (Shah et al., 2004), ortho-substituted aniline-N-salicylidenes (Desai et al., 2003), ortho-, meta-, and para-aminophenol-N-salicylidenes (Talati et al., 2005b), and meta-substituted aniline-N-salicylidenes (Talati et al., 2005a) has been reported.

In the present work, the inhibitive effectiveness of o-CANB has been studied in retarding corrosion of Al-Pure in 1.0 M HCl. Weight loss method, galvanostatic polarization and electrochemical impedance spectroscopy (EIS) technique were used to investigate the inhibiting influence of o-CANB.

2. Experimental details

The Schiff base compound was synthesized from an equimolar amount of benzaldehyde and corresponding amine (o-Chloroaniline) through a condensation reaction in ethanol media. The chemical structure of used Schiff base is characterized by IR (Fig. 1), which is shown below:



o-CANB

Rectangular specimens of Al-Pure, of size 6.0 cm × 3.0 cm (thickness = 0.050 cm), were polished to mirror finish, degreased with A.R. carbon tetrachloride (sulfur free), and used for the weight loss method. The specimens were immersed in 230 ml of the solution containing various concentrations of the inhibitor in the absence and presence of o-CANB, at 35 ± 0.5 °C for an exposure period of 60 min. The weight of the specimen before and after immersion was determined using a mettler balance – M5 type. The accuracy of the balance was 0.0001. Triplicate experiments were performed. After completing weight loss experiments the metal coupon was washed with double distilled water, dried and weighed. Experiments (the loss in weight of specimen) were carried out at 0.5% concentration of the inhibitor at temperatures ranging from 35 ± 0.5 °C to 65 ± 0.5 °C.

For polarization and EIS studies, metal coupons of circular design, diameter 2.802 cm with a handle 3 cm long and 0.5 cm wide were used. The handle and the back of the coupon and of the auxiliary platinum electrode were coated with Perspex leaving only the circular portion of the specimen exposed to the apparent surface area, 6.156 cm^2.

Polarization and EIS studies were carried out using a three electrode cell assembly, Al-Pure was used as a working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as the reference electrode. Corrosion current densities (I_{corr}) and corrosion potentials (E_{corr}) were evaluated from the intersection of the linear cathodic and anodic Tafel plots of the polarization curves in polarization study. In this study, the current density was varied in the range of 2×10^{-4}–3.25×10^{-2} A cm^{-2}. Electrochemical impedance measurement was carried out in the frequency range of 20 kHz–0.1 Hz at the open circuit potential, after 1 h (60 min) of immersion, by applying an amplitude of 5 mV sine wave ac signal (AUTOLAB). Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values were calculated from Nyquist plots as described by Hosseini et al. (2003). EIS data were analyzed using a frequency response analyzer (FRA) electrochemical setup.

3. Results and discussion

3.1. Influence of inhibitor concentration on the corrosion rate and Inhibition efficiency

In the absence and presence of o-CANB, the rate of corrosion was studied using a weight loss method on Al-Pure at 35 ± 0.5 °C. The calculated values of inhibition efficiency (%IE) and the degree of surface coverage (θ) are shown in Table 1. The results show that the inhibitor inhibited the corrosion of Al-Pure in 1.0 M HCl at 35 ± 0.5 °C for an exposure period of 60 min. Increasing the concentration of o-CANB, increases in the inhibition efficiency (%IE) upto a maximum value of >99% at 0.5% inhibition concentration. Therefore, we can say that the inhibition was found to depend on inhibitor's concentration. The inhibitory action of o-CANB against Al-Pure corrosion can be attributed to the adsorption of its molecules on Al-Pure surface, which limits the dissolution of the latter by blocking its corrosion sites and hence decreasing the weight loss, with increasing efficiency as the concentration increases.

The percentage inhibition efficiency (%IE) and the degree of surface coverage (θ) were calculated using following equations:

$$\text{Inhibition efficiency } (\%\text{IE}) = \frac{W_u - W_i}{W_u} \times 100 \quad (1)$$

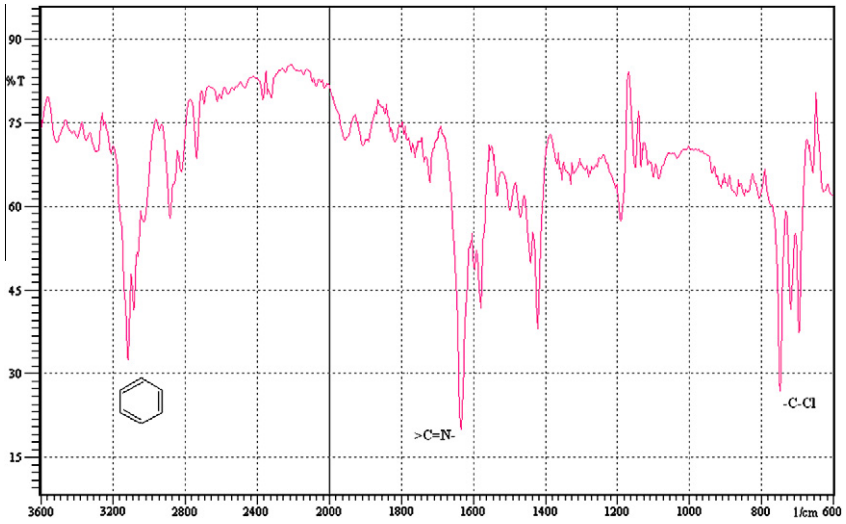


Figure 1 IR spectra of o-CANB.

Table 1 Corrosion parameters for Al-pure in the presence and absence of different concentrations of Schiff base obtained from weight loss measurement at 35 ± 0.5 °C for an exposure period of 60 min.

Inhibitor	Concentration (% V/V)	Weight loss (mg dm^{-2})	Surface coverage (θ)	(%IE)
Blank	–	2300	–	–
o-CANB	0.001	683	0.7030	70.3
	0.01	442	0.8078	80.8
	0.05	260	0.8869	88.7
	0.10	138	0.9400	94.0
	0.50	14	0.9939	99.4

$$\theta = \frac{W_u - W_i}{W_u} \quad (2)$$

where W_u = weight loss of Al-Pure in uninhibited acid and W_i = weight loss of Al-Pure in inhibited acid.

3.2. Adsorption isotherm

The adsorption of the inhibitor at the metal/surface interface is the first step in the inhibition mechanism in aggressive media. There are three types of possibilities of adsorption that may take place by organic molecules at the metal/solution interface: (i) electrostatic attraction between the charged metal and the charged molecules, (ii) interaction of π-electrons with the metal and (iii) combination of [(i) and (ii)] (Obot and Obi-Egbedi, 2008). The adsorption isotherms are useful for acknowledging the mechanism of corrosion inhibition.

The values of surface coverage (θ) (given in Table 1) for the different concentrations of the studied inhibitor at 35 ± 0.5 °C have been used to explain the best adsorption isotherm to determine the adsorption process. Attempts were made to fit θ values of various isotherms including Langmuir, Temkin and Freundlich isotherms. Among the three isotherms obtained the best fitted was the Langmuir adsorption isotherm. Plotting of log ($\theta/(1-\theta)$) against log C_{inh} gave a straight line (Fig. 2), indicating that the adsorption of Schiff base compound on Al-Pure surface follows the Langmuir isotherm.

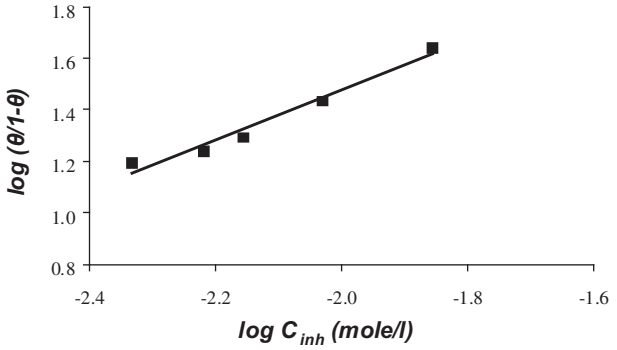


Figure 2 Langmuir isotherm for the adsorption of o-CANB on the Al-Pure metal surface.

3.3. Effect of temperature and thermodynamic parameters

To study the effect of temperature on the inhibition efficiency, weight losses were determined at 35 °C, 45 °C, 55 °C and 65 °C in 1.0 M HCl, uninhibited as well as inhibited. The results given in Table 2 show that the inhibition efficiency increases with inhibitor concentration but decreases with temperature. Increasing of inhibition efficiency with the increase of inhibitor concentration indicates that, this compound is acting as an adsorption inhibitor. But decrease in inhibition efficiency with increase in temperature can be ex-

Table 2 Effect of temperature on weight loss and inhibition efficiency for Al-Pure in 1.0 M hydrochloric acid.

Inhibitor	Concentration (% V/V)	Weight loss (mg dm^{-2}) at temperature			
		35 °C	45 °C	55 °C	65 °C
Blank	–	2300	4436	5303	5808
o-CANB	0.5	14 (99.4%)	41 (99.1%)	98 (98.2%)	198 (96.6%)

plained by desorption of inhibitor molecules on the metal surface at higher temperatures.

The activation parameters for the corrosion process can be evaluated from the Arrhenius-type plot according to the following equation (Joseph et al., 2010):

$$\rho = k \exp\left(-E_a/RT\right) \tag{3}$$

where ρ is the corrosion rate, E_a is the activation energy, T is the temperature and k is the constant. Plotting log ρ versus $T^{-1} \times 10^4$ gave a straight line with a slope of $-E_a/R$ (Fig. 3). Calculated activation energies are given in Table 3. The observed increase in activation energy in the presence of o-CANB from 25.9 kJ mol^{-1} (value of uninhibited E_a) to 79.9 kJ mol^{-1} (value of inhibited E_a) with an attendant decrease in inhibition efficiency of the inhibitor as temperature increases suggests physical adsorption of the inhibitor molecules on the metal surface (Ostovari et al., 2009).

If it is assumed that the inhibitor is adsorbed on the metal surface in the form of a monolayer film, covering at any instant a fraction, θ, of the metal surface in a uniform random manner, then the heat of adsorption, (Q_{ads}), of the inhibitor can be calculated from the equation:

$$Q_{ads} = 2.303R\left\{\log\frac{\theta_2}{1-\theta_2} - \log\frac{\theta_1}{1-\theta_1}\right\}\left(\frac{T_1T_2}{T_2-T_1}\right) \tag{4}$$

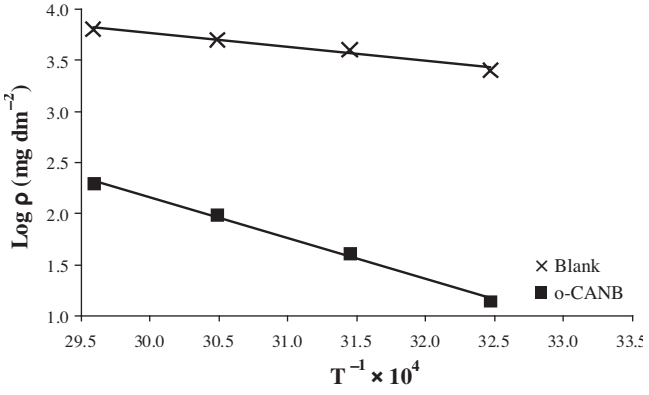


Figure 3 Plotting log ρ vs. $T^{-1} \times 10^4$ to calculate the activation energy of corrosion process in the presence and absence of o-CANB.

Table 3 Thermodynamic parameters and activation energy for inhibitor adsorption for corrosion of Al-Pure in 1.0 M HCl.

Inhibitor	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	ΔG_{ads} (kJ mol^{-1})
Blank	25.9	–	–
o-CANB	79.9	−51.9	−32.6

The values of the free energy of adsorption (ΔG_{ads}) were calculated from the following equation (Desai et al., 2008):

$$\log C_{inh} = \log\frac{\theta}{1-\theta} - \log B \tag{5}$$

$$\text{where,}\quad \log B = -1.74 - (\Delta G_{ads}/2.303RT) \tag{6}$$

The values of (ΔG_{ads}) and (Q_{ads}) are shown in Table 3. The negative value of (ΔG_{ads}) suggests that the inhibitor molecules are strongly adsorbed on the metal surface, the value also indicates a spontaneous adsorption of the inhibitor molecules usually characterized by the strong interactions with the metal surface. It is found that the (ΔG_{ads}) values around −20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physisorption); those around −40 kJ mol^{-1} or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) (Noor and Al-Moubaraki, 2008). In the present work, the calculated (ΔG_{ads}) value is less negative than −40 kJ mol^{-1} indicating that the adsorption of inhibitor molecules is of the physisorption type.

The negative value Q_{ads} indicated that the adsorption of used inhibitor on the aluminium surface is exothermic (Ashassi-Sorkhabi et al., 2006).

3.4. Polarization study

The galvanostatic polarization curves of Al-Pure in 1.0 M HCl in the presence and absence of two concentrations of o-CANB are shown in Fig. 4, and it was observed that in the presence of the inhibitor, both of the cathodic and anodic curves show lower current density than those observed in the uninhibited solution. This behavior indicated that the Schiff base has an effect on both the cathodic and anodic reactions of the corrosion process. Therefore, this compound could be classified as a mixed type inhibitor at lower inhibitor concentrations. The inhibitor shifts the potential in the negative direction; this effect is more evident at higher concentrations, which means that the inhibitor affect the cathodic reaction more than the anodic reaction at higher concentrations. The values of cathodic Tafel slope (b_c) and anodic Tafel slope (b_a) calculated from the linear region of the polarization curves are given in Table 4. The corrosion current density (I_{corr}) was determined from the intersection of the linear parts of the cathodic curves with stationary corrosion potential (E_{corr}).

The percentage inhibition efficiency (%IE) was calculated using the following equation:

$$(\%IE) = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \tag{7}$$

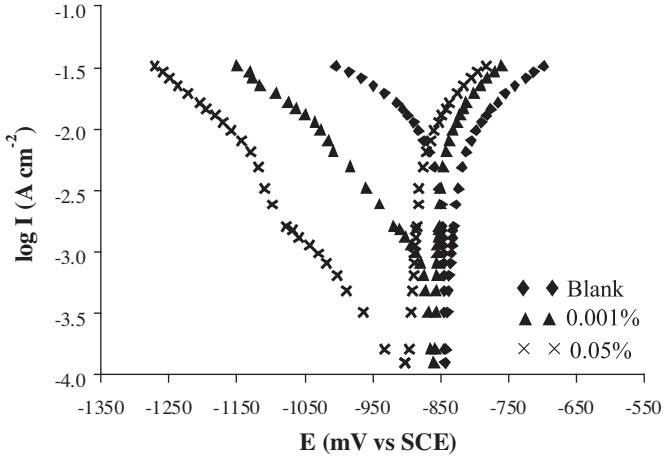


Figure 4 Anodic and cathodic polarization curves obtained for Al-Pure metal at 35 ± 0.5 °C in 1.0 M HCl in various concentration of o-CANB.

Table 4 Electrochemical parameter of corrosion of Al-Pure in the presence of two different concentrations of the inhibitor at 35 ± 0.5 °C and corresponding inhibition efficiency obtained from the polarization method.

Inhibitor	Concentration (%V/V)	E_{corr} (mV)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} for cathodic (A cm^{-2})	(%IE)
Blank	–	−843	113	120	4.467×10^{-3}	–
o-CANB	0.001	−860	59	136	0.617×10^{-3}	86.1
	0.05	−902	68	162	0.281×10^{-3}	93.7

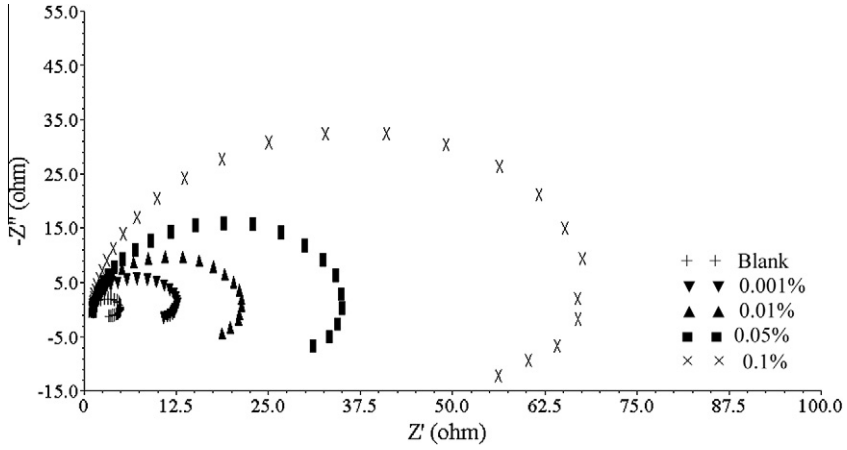


Figure 5 Impedance plot obtained at 35 °C in 1.0 M HCl in various concentrations of o-CANB.

where I^0_{corr} and I_{corr} are the corrosion current densities in the absence and presence of the inhibitor.

3.5. Electrochemical impedance spectroscopy (EIS)

Nyquist plots of Al-Pure in 1.0 M HCl solution in the absence and the presence of various concentrations of o-CANB are given in Fig. 5. It is clear from the figure that the impedance diagram obtains yield a semi-circle shape. This indicates that the corrosion process is mainly controlled by charge transfer.

The equivalent circuit fitting for the experimental data was a Randles circuit. The Randles equivalent circuit is one of the simplest and most common circuit models of electrochemical impedance. It includes a solution resistance R_s, in series to a parallel combination of resistor, R_{ct},, the charge transfer (corrosion) resistance and a double layer capacitance, C_{dl}, respectively, the electrode capacitance (Yagan et al., 2006). In this case, R_s values can be neglected because the value is

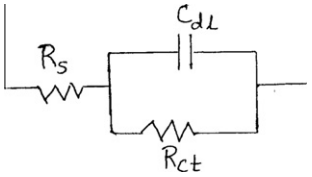


Figure 6 The equivalent circuit model used to fit the experimental results.

Table 5 Impedance parameters and corresponding inhibition efficiency for the corrosion of Al-Pure in the 1.0 M HCl.

Inhibitor	Concentration (%V/V)	R_s (Ω)	R_{ct} (Ω)	C_{dl} (μF)	(%IE)
Blank	–	1.079	3.99	85.7	–
o-CANB	0.001	1.317	12.5	82.6	68.2
	0.01	1.161	20.8	77.7	80.8
	0.05	1.359	33.7	74.2	88.1
	0.10	1.072	68.8	68.7	94.2

too small as compact to that of the value of R_{ct}. The equivalent circuit for the Randles cell is shown in Fig. 6.

The FRA (frequency response analyzer) is used for impedance data analysis and the fit parameters are listed in Table 5. where R_{ct}, R_s and C_{dl} are the charge transfer resistance, solution resistance and double layer capacitance, respectively. From the impedance measurements, inhibition efficiency was calculated using the following expression:

$$(\%\mathrm{IE}) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (8)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistances of the electrode with and without the inhibitor, respectively. The result shows that, R_{ct} values increase with increasing the inhibitor's concentration. On the other hand, the values of C_{dl} decrease with increasing the inhibitor's concentration. This is due to the increasing surface coverage by the inhibitor, which leads to an increase in the inhibition efficiency with increasing inhibitor concentration. The electrochemical theory shows that C_{dl} is proportional to the corrosion rate (Ashassi-Sorkhabi et al., 2006).

3.6. Mechanism of the inhibition

Many organic corrosion inhibitors are compounds with at least one polar unit containing atoms of nitrogen, sulfur, oxygen and in some cases selenium and phosphorous. The polar unit is regarded as the reaction centre for the establishment of the adsorption process and the adsorption bond strength is determined by the electron density on the atom acting as the reaction centre and by the polarizability of the fundamental unit (Patel et al., 2010).

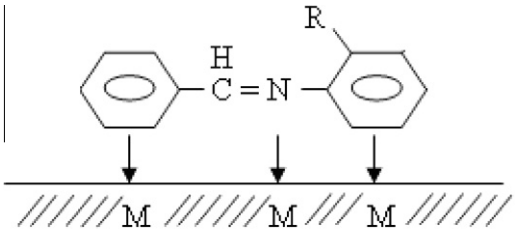
Amine-type inhibitors have electron-donating ability and their action is attributed to the adsorption of the molecule on the metal surface through an unshared pair of electrons belonging to the nitrogen atom (Shah et al., 2011). The inhibitor molecules are adsorbed chemically on the surface of the bulk metal, M, forming a charge transfer complex between the polar atom/atoms and the metal,

$$\mathrm{M} + \mathrm{RnX} \leftrightarrow \mathrm{M} : \mathrm{XRn} \quad (9)$$

where M is the metal, X is the ligand or polar atom, Rn is the subsisted group on the polar atom or ligand.

Further, this inhibitor, which is in a distinct ionic form, also may get attached to the metal surface of opposite polarity through electrostatic attraction. The adsorbed layer then will block the dissolution of the metal. The size, orientation and shape of the molecule, and the electronic charge on it, will determine the degree of adsorption and hence the effectiveness of the inhibitor.

o-CANB contains seven conjugated double bonds (six in the aromatic ring + one iminic). The adsorption takes place due to the iminic group. It is also possible that the compounds may form onium ions in acidic medium and move to the cathodic regions and then the adsorption will take place through the iminic nitrogen and also through the delocalized π-electrons of the benzene moiety. Then molecule will lie flat on the metal surface and further cover the adjoining positions of the surface.



Where, R = –Cl in o-CANB

4. Conclusions

- Results obtained from the experimental data show o-CANB inhibitor is an effective inhibitor for the corrosion of Al-Pure in 1.0 M HCl. Inhibition efficiency increases with an increase in the concentration of the studied inhibitor but decreases with a rise in temperature.
- The adsorption of o-CANB on Al-Pure surface from 1.0 M HCl obeys the Langmuir adsorption isotherm.
- The phenomenon of physical adsorption is proposed from the values of thermodynamic parameters (E_a, ΔG_{ads}) obtained for o-CANB.
- Schiff base acts as a mixed type inhibitor with predominant action on cathode and its inhibition efficiency tends to increase with increasing inhibitor concentration.
- The EIS measurement clarified that the value of R_{ct} increased with the addition of the inhibitor, while the C_{dl} value decreased, indicating the formation of a surface film.
- Obtained results about inhibition efficiency from weight loss, polarization study and EIS are in good agreement with each other.

Acknowledgments

The authors are grateful to the Chemistry Department, School of Sciences, Gujarat University, Gujarat, for laboratory facility. Two of the authors Aesha Patel and Vidhi Panchal are also thankful to UGC-BSR for Research fellowship.

References

Abd El-Maksoud, S.A., 2002. Corros. Sci. 44, 803.

Addel-Gaber, A.M., Abd-El-Nabey, B.A., Sidahmed, I.M., El-Zayady, A.M., Saadawy, M., 2006. Mater. Chem. Phys. 98, 291.

Ajmal, M., Mideen, A.S., Quraishi, M.A., 1994. Corros. Sci. 36, 79.

Ashassi-Sorkhabi, H., Shabani, B., Aligholipour, B., Seifzadeh, D., 2006. Appl. Surf. Sci. 252, 4039.

Aytac, A., Ozmen, U., Kabasakaloglu, M., 2005. Mater. Chem. Phys. 89, 176.

Bain, C.D., Throughton, E.B., Tao, Y.T., Evall, J., Whiteside, G.M., Nuzzo, J.G., 1989. J. Am. Soc. 111, 321.

Desai, M.N., Desai, M.B., Shah, C.B., Desai, S.M., 1986. Corros. Sci. 26, 827.

Desai, M.N., Talati, J.D., Shah, N.K., 2003. Ind. J. Chem. 42A (12), 3027.

Desai, M.N., Talati, J.D., Shah, N.K., 2008. Anti-Corros. Meth. Mater. 55 (1), 27.

Emregul, K.C., Kurtaran, R., Atakol, O., 2003. Corros. Sci. 45, 2803.

Gomma, G.K., Wahdan, M.H., 1995. Mater. Chem. Phys. 39, 209.

Hahner, G., Woll, Ch., Buck, M., Grunze, M., 1993. Langmuir 9 (1), 955.

Hosseini, M.G., Mertens, S.F.L., Gorbani, M., Arshadi, M.R., 2003. Mater. Chem. Phys. 78, 800.

Joseph, B., John, S., Abraham, J., Narayana, B., 2010. Ind. J. Chem. Technol. 17, 366.

Li, S.L., Chen, S., Lei, S.B., Ma, H., Yu, R., Liu, D., 1999. Corros. Sci. 41, 1273.

Noor, E.A., Al-Moubaraki, A.H., 2008. Mater. Chem. Phys. 110, 145.

Obot, I.B., Obi-Egbedi, N.O., 2008. Colloid Surf. A 330, 207.

Ostovari, A., Hoseinieh, S.M., Peikari, M., Shadizadeh, S.R., Hashemi, S.J., 2009. Corros. Sci. 51, 1935.

Patel, A.S., Panchal, V.A., Shah, N.K., 2010. J. Pure Appl. Sci. 18, 73.

Pourbaix, M., 1966. Atlas of electrochemica. Equilibria in Aqueous Solutions. Pergamon press, New York.

Rosliza, R., Wan Nik, W.B., Izman, S., Prawoto, Y., 2010. Curr. Appl. Phys. 10, 923.

Shah, N.K., Agrawal, Y.K., Talati, J.D., Shah, M.D., Desai, M.N., 2004. Corros. Sci. 46 (3), 633.

Shah, M.D., Panchal, V.A., Mudaliar, G.V., Shah, N.K., 2011. Anticorros. Meth. Mater. 58 (3), 125.

Talati, J.D., Desai, M.N., Shah, N.K., 2005a. Mater. Chem. Phys. 93 (1), 54.

Talati, J.D., Desai, M.N., Shah, N.K., 2005b. Meth. Mater. 52 (2), 108.

Yagan, A., Pekmez, NO., Yildiz, A., 2006. Prog. Org. Coat. 57, 314.

Yurt, A., Ulutas, S., Dal, H., 2006. Appl. Surf. Sci. 253, 919.